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NATIONAL BUREAU OF STANDARDS REPORT

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AIR BLOWING ASPHALTS IN THE PRESENCE OF ADDITIVE OILS, CATALYSTS AND POLYMERS

by

Sidney H. Greenfeld

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U. S. DEPARTMENT OF COMMERCE
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Asphalt Roofing Industry Bureau

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Sidney H. Greenfeld

1. INTRODUCTION

Bitumen has been used for many centuries in a wide variety of waterproofing applications. For the first 5000 years of its use by man, it was applied essentially as it came from nature. Bitumens from various sources were more-or-less in demand because of their special properties. However, in the second half of the nineteenth century, organized efforts were first made to modify bitumens by various processes and treatments and divorce the dependence of their end uses from their sources.

In 1894 (1)[a], the first commercial process for the modification of asphalt by air blowing was patented by F. X. Byerley. This patent described a rather crude process for drawing air through petroleum residua to harden these residua. Although the process has been modified and improved many times, it still has its limitations for changing the properties of bitumens. In recent years, a number of publications have appeared, which describe the effect of various processing variables, such as air rate, temperature, agitation and still design, on the properties of blown asphalts (2). In all instances the improvements in properties were limited by the composition of the flux which was blown.

Asphalt producers have been concerned with these limitations and have tried numerous additives during the blowing process to produce asphalts with desired properties. Amond the earlier modifying endeavors was the blending of crudes or residua to produce fluxes that would air-blow to the required specifications (3). Oils, called fluxing oils, and other organic products were added either before or after blowing to produce products with higher penetrations for a given softening point. Many varieties of inorganic and organic compounds have been used to make specific adjustements in a given asphalt (4, 5). Abraham (4) reports many patents issued on these various treatments and Mertens and Greenfeld (5) have shown that a given agent may be beneficial to asphalt from one source and detrimental to asphalts from another.

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[a] Numbers in parentheses refer to the references listed at the end of this paper.

With all of the claims and counter claims in the patent literature and only a few publications with substantiating data for the effects of additives during blowing on the properties of blown asphalts, it seemed that further investigation of this phase was in order. The effects of a selected few representative additives on the blowing characteristics of four fluxes and on the properties of the blown asphalts were studied. The fluxes were those the blowing characteristics of which have been reported (2f).

2. MATERIALS

The physical properties of the fluxes used in this program are tabulated in Table 1. The California flux was supplied in one grade only; each of the other three was supplied in two grades. The softer grade was selected such that it could be blown to coating softening point-penetration requirements without modification. The harder grade was selected to require modification to meet this specification. In practice, however, the harder grades of these three fluxes could be blown to these requirements under certain processing conditions without the use of additives.

The California flux could not be obtained sufficiently soft to permit blowing to coating requirements. The limiting factor was the flash point; the crude was reduced to a flash point of 460°F (COC) to permit safe handling. A discussion of the effects of processing variables on this California flux and the soft fluxes from the other three sources has been published (2f).

A number of materials were added to the asphalt fluxes prior to blowing. These materials are described in Table 2.

3. APPARATUS AND PROCEDURE

The apparatus used for blowing the asphalts and determining their durabilities are those described previously (2f). In the runs in which the flux-additive mixtures were blown without agitation, the additives were mixed with the fluxes externally with the aid of a laboratory stirrer. The mixtures were added to the stills at 300-350°F. In the runs in which agitation was used, the additives were mixed with the fluxes in the stills with the aid of the agitators. All fluxes were blown at 465-475°F, 0 or 1400 rpm agitation and 75 or 150 ft^3/ton-min. air rate as reported. Initially the lower air rate had been arbitrarily selected, but because

TABLE I.

ASPHALT FLUXES

Flux	California Coastal	Kansas		Talco		Tia Juana	
		Soft	Hard	Soft	Hard	Soft[1]	Hard
Softening Point, °F	122	101	120	104	120	104	111
Penetration at 32°F, 0.1 mm	20	42	18	44	27	44	25
Penetration at 77°F, 0.1 mm	64	249	80	190	92	152	91
Penetration at 115°F, 0.1 mm	TS[2]	TS	TS	TS	TS	222	232
Specific Gravity at 77°F	1.030	0.994	1.004	1.020	1.022	1.004	1.011
Flash Point (C.O.C.), °F	460	635	645	555	560	575	620
Asphaltenes, %	30.7	19.3	24.9	26.7	28.1	23.4	20.8
Sulfur, %	5.6	1.4	1.4	4.6	4.8	2.9	3.1

[1] Partially blown

[2] Too Soft

TABLE 2. ADDITIVES

OILS

Material	Flash Point (COC) °F	Viscosity at 210°F SSU	Pour Point, °F
Mid Continent Bright Stock	600	160	5
Western Bright Stock	615	196	10
Western Reclaimed Lube Oil	440	68	-
Eastern Reclaimed Lube Oil	460	61	-

"CATALYSTS"

Material	Form	Manufacturer	Designation
Ferric Chloride	Hexahydrate	Baker & Adamson Company	Reagent
Phosphoric Acid	86% Solution	Baker & Adamson Company	Reagent
Phytic Acid	70% Solution	A. E. Staley Mfg. Co.	-
Pyromellitic Dianhydride (PMDA)	White Powder	E. I. duPont de Nemours & Co.	Experimental Sample
Trimellitic Anhydride (TMA)	White Powder	Amoco Chemicals Corp.	Experimental Products
VR-1 Acid [1]	Brown Liquid	Rohm and Haas	-

[1] By-product of manufacture of sebacic acid from castor oil. Ratio of dibasic to monobasic acids = 1.2.

POLYMERS

Polymer	Form	Manufacturer	Manufacturer's Designation
Neoprene	Latex 66% Solids	E. I. duPont de Nemours & Co.	LD-260
Silicone	Liquid & Catalyst	Dow-Corning	RTV-521
Epoxy	50% Epoxy Liquid	Dow Chemical Company	DER 332
	50% Amide Liquid	General Mills, Inc.	Versamid 140
Polyvinyl Formal	Powder	Shawinigan Resins Corp.	Formvar 7/95S
Polyvinyl Butral	Powder	Shawinigan Resins Corp.	Butvar 72A

some runs could not be completed in one day, the higher rate was adopted for the later runs.

Softening points and penetrations (2f) were determined on each asphalt produced. The change in softening point was used to follow the progress of the blowing process; the penetrations were measured only on the finished products.

All of the asphalts were exposed in two weatherometers, two specimens of each in each machine. The figures reported are the averages of these four specimens. In a few instances these replicates failed widely apart; second sets of four specimens were exposed.

4. RESULTS

The blowing conditions and physical properties of asphalts blown without additives are summarized in Table 3. These results are used in comparisons with the modified coatings and are compiled in Table 3 to demonstrate the variations in properties and durabilities that can be expected from variations in the flux and blowing conditions.

Tables 4, 6 and 7 are summaries of the effects of fluxing oils, catalysts and polymers, respectively, on the physical properties of the blown asphalts. Table 8 contains the durability data on all three of these systems.

5. DISCUSSION

The roofing manufacturer and the asphalt refiner, to a lesser extent, are usually limited by economic considerations to a choice from a relatively few asphalt fluxes. Occasionally normal processing of these fluxes produces products of somewhat less-than-desired quality. The question always arises concerning how the best qualities can be produced within economic reason.

In 1957, it was reported that blown asphalts from a particular flux decreased in durability as the softening point increased (6). In 1964, it was shown that by suitably changing one or more of the processing variables (temperature, air rate or agitation), asphalts could

TABLE 3.

PROPERTIES OF UNMODIFIED ASPHALTS

Flux Composition	Air Rate ft^3/TM	Agitation R.P.M.	Blowing Time Min.	S.P. °F	Penetrations at 32°F 1/10 mm	Penetrations at 77°F 1/10 mm	Penetrations at 115°F 1/10 mm	Susceptibility $\frac{P115-P32}{P77}$	Durability Days
California	75	0	300	223	4	9	17	1.5	44
"	150	0	240	217	4	8	18	1.8	44
"	75	1400	69	221	7	12	26	1.6	62
"	150	1400	61	223	6	16	25	1.2	67
Kansas (Soft)	150	0	330	221	11	19	29	1.0	65
" (Hard)	150	0	202	219	9	18	36	1.5	81
" (Soft)	75	1400	81	219	12	21	36	1.1	81
" (Hard)	75	1400	62	219	12	19	34	1.3	100
" (Soft)	150	1400	68	221	12	20	34	1.1	73
" (Soft)	75	0	562	217	12	21	34	1.0	87
Talco (Soft)	150	0	317	219	12	19	36	1.3	56
" (Hard)	150	0	212	219	12	17	32	1.2	57
" (Soft)	75	1400	65	217	13	20	34	1.1	48
" (Hard)	75	1400	61	217	11	18	35	1.3	62
" (Soft)	150	1400	55	219	12	20	32	1.0	47
" (Soft)	75	0	600	219	11	17	33	1.3	45
Tia Juana (Soft)	75	0	390	217	14	21	38	1.1	59
" " (Hard)	75	0	374	217	9	16	30	1.3	68
" " (Soft)	75	1400	64	217	14	21	37	1.1	50
" " (Hard)	75	1400	68	219	11	16	31	1.3	80
" " (Soft)	150	0	206	217	14	22	39	1.1	60
" " (Soft)	150	1400	56	217	13	22	37	1.1	52

be blown to the same softening point with large variations in durability and production time and lesser variations in penetrations (2f). Table 3 shows still another way of changing the softening point-penetration relation and the durabilities of asphalts. While not specifically designed as a part of this study, this consideration is sufficiently important to the discussion of the results to be considered before the discussion. It was found that asphalts blown from fluxes which came from the same batch of crude, but reduced to different extents, were different both in physical properties and in durability. As might be expected, the asphalts produced from the harder fluxes had lower penetrations than those produced from the corresponding softer fluxes blown under the same conditions. The blowing times in all but one instance were also shorter. However, despite the poorer properties, the asphalts produced from the harder fluxes were invariably, and in many cases appreciably, more durable[b/]. From these results it would seem that crude reduction to the greatest extent consistent with the production of a flux that can be blown to coating-grade specifications is desirable for durability as well as flash point considerations.

Because of the flash point restrictions, the California flux could not be supplied in a sufficiently soft grade to permit blowing to coating grade without modification. This point was discussed in detail in reference (2f). Thus, reference California asphalts could not be produced within coating-grade specifications. Very few of the additives were capable of modifying this flux sufficiently to permit the production of specification coating-grade asphalts from it.

One of the most generally used and widely acceptable procedures used to modify coating-grade asphalts is to dilute, or flux, the material charged to the blowing still with an oil. The oils used range from reclaimed lubricating oil through various refinery distillates to heavy residual materials, which in themselves may be considered asphalt fluxes. It is quite difficult to obtain what might be termed representative materials because of the unlimited number available. Therefore, only a limited sampling of two of the more-common types of oil were evaluated; two samples of each were used.

[b/] There is some question concerning the exact processing of the Tia Juana Medium soft flux. It is believed that this material was partially blown by the refinery.

TABLE 4.

EFFECT OF FLUXING OILS ON PHYSICAL PROPERTIES OF ASPHALTS

Flux Composition	Blown Without Agitation at 475°F, 150 ft^3/Ton Min					Blown With Agitation at 475°F, 150 ft^3/Ton Min				
			Penetrations					Penetrations		
	Time Min.	S.P. °F	at 32°F 1/10 mm	at 77°F 1/10 mm	at 115°F 1/10 mm	Time Min.	S.P. °F	at 32°F 1/10 mm	at 77°F 1/10 mm	at 115°F 1/10 mm
California	240	217	4	8	18	69[1]	221	7	12	26
+ 5% ERL	181	219	9	15	32	60[1]	217	11	16	34
+ 5% WRL	263	217	7	14	30	63[1]	219	10	17	31
+ 5% MCBS	214	217	9	16	27	40[1]	221	9	13	26
+ 5% WBS	226	217	8	13	27	60[1]	219	10	15	28
Kansas (Hard)	202	219	9	18	36	62[1]	219	12	19	34
+ 5% ERL	230	221	14	21	34	65[1]	219	13	21	30
+ 5% WRL	304	219	12	19	32	71[1]	217	13	22	33
+ 5% MCBS	170	217	12	20	38	65[1]	217	12	21	30
+ 5% WBS	248	217	12	19	33	73[1]	221	12	20	28
Kansas (Soft)	330	221	11	19	29	81[1]	219	12	21	36
Talco (Hard)	212	219	12	17	32	61[1]	217	11	18	35
+ 5% ERL	290	218	12	17	32	77	223	12	19	34
+ 5% WRL	312	217	12	17	34	77[1]	219	12	18	32
+ 5% MCBS	300	217	12	19	36	66	217	12	20	31
+ 5% WBS	296	217	12	18	36	76[1]	221	11	19	30
Talco (Soft)	317	219	12	19	36	65[1]	217	13	20	34
Tia Juana (Hard)	374[1]	217	9	16	30	68[1]	219	11	16	31
+ 5% ERL	465[1]	219	11	21	35	68[1]	217	13	22	40
+ 5% WRL	540[1]	217	10	18	33	71[1]	217	12	20	35
+ 5% MCBS	525[1]	219	12	18	32	67[1]	217	12	21	34
+ 5% WBS	540[1]	219	11	17	30	72[1]	220	12	19	32
Tia Juana (Soft)	390[1]	218	13	21	38	64[1]	217	13	21	37

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[1] Air Rate of 75 ft^3/Ton Min

The two Bright Stock oils are high-viscosity-index distillate oils, one from a Mid-Continent crude segregation and one from a California coastal segregation, both of which are normally used as base materials with which additives are mixed to produce premium motor oils. They are paraffinic in nature; the aromatics, unsaturates and waxes have been largely removed through solvent extraction and dewaxing processes. Their name is descriptive of their bright, clear appearance in contrast to the cloudy, dark color of the straight distillate oils.

The eastern and western reclaimed lubricating oils are crank case drainings, which have been filtered to remove sludge and solids and topped to remove all light materials and water. They are dark in color, almost as if they have finely divided, suspended carbon present.

The effects of the addition of 5% of each of these oils to each of the hard fluxes before blowing are shown in Table 4. The blowing characteristics of the unmodified fluxes are reproduced for easy comparison in this and the following tables. In order to provide a basis for discussion and a plane of reference, the specification for a hypothetical asphalt presented in reference (2f) is reproduced in Table 5. It should be recalled that this specification is not one used by any one manufacturer, but is one that tends to bracket, or include, a large number of specifications in current use.

TABLE 5.

SPECIFICATION FOR A HYPOTHETICAL COATING-GRADE ASPHALT

Property	Range
Softening Point, °F	215-225
Penetration at 32°F, 1/10 mm	10 minimum
Penetration at 77°F, 1/10 mm	15-25
Penetration at 115°F, 1/10 mm	25-45

It is quite obvious from Table 4 that blown asphalts meeting this specification were not produced from the California flux without modification either with or without agitation. The use of agitation, with a much-shorter residence time in the still, produced a product of considerably improved penetrations over the one produced without agitation, but still short of the specification. None of the fluxing oils at the 5% level

was able to improve the penetrations sufficiently in the absence of agitation to make the grade, but both the Eastern Reclaimed Lube Oil and Mid-Continent Bright Stock were close. However, neither of these oils is available in areas in which this flux is used. A larger percentage of the western oils would have to be used to accomplish the same effects.

When agitation was used along with the fluxing oils, all except the Mid-Continent Bright Stock increased the penetrations sufficiently to meet the specification in Table 5. Despite the addition of these oils, the blowing times were shorter in all of these runs than for the unmodified flux.

The soft Kansas flux blew into grade whether or not agitation was used; the hard flux, only when agitation was used. However, without agitation the coating-grade product failed to meet the specification by only one penetration unit at 32°F. All of the modified fluxes produced specification products. Unlike the modified California fluxes, all but one of the modified Kansas fluxes blew into grade more slowly than did the hard flux. (The run without agitation using Mid-Continent Bright Stock was the exception). However, these runs were shorter than when the soft flux was used alone. The high-temperature penetrations seemed to benefit least from the fluxing oils, and, in most instances, were actually lower than the coating asphalt produced from the hard flux without modification.

The reclaimed lubricating oils had almost no effect on the penetrations of the asphalts produced from the Talco flux, but the Bright Stocks changed the high temperature penetrations. Without agitation, the penetrations at 115°F were raised; with agitation, they were lowered. All of the fluxing oils increased the blowing times required to make coating asphalts from the hard Talco flux.

The penetrations of the coating asphalts produced from 5% of each of the fluxing oils in the hard Tia Juana flux were increased. This flux produced asphalts that were marginally acceptable without fluxing oils and well within the specification range with them. The blowing times were increased appreciably in the absence of agitation, but only slightly when agitation was used.

From this discussion, it is quite obvious that the fluxing oils and base stocks must be carefully paired in order to improve the physical characteristics of the coating asphalt produced. While lowering of the penetrations occurred only infrequently, many combinations produced little improvement and quite frequently the improvement was obtained at the expense of an increase in blowing time.

The effects of these fluxing oils on the durabilities of coating asphalts were also extremely variable. The largest improvements were manifested by the western oils in the Talco asphalts blown without agitation. This flux produced asphalts with durabilities in the range of 32-56 days (2f) under a wide variety of processing conditions, but with these fluxing oils durabilities of 85 days were obtained. Again, these western oils are not normally available in areas in which Talco flux is processed, but the Mid-Continent Bright Stock and similar oils are and produce comparable improvements in durability.

The Western Bright Stock and Reclaimed Lubricating Oil and Mid-Continent Bright Stock also improved the California asphalts blown without agitation. These asphalts had durabilities comparable to the best California asphalts produced with agitation. However, these same oils were not beneficial when agitation was used.

When the Kansas flux was blown with 5% of each of the fluxing oils without agitation, there was marked improvement in each case over the asphalt from the soft flux, but the asphalt produced with the Eastern Reclaimed Lubricating Oil was not as durable as the asphalt produced from the hard Kansas flux. When agitation was used, the Eastern Reclaimed Lube was definitely detrimental and, while the use of the other fluxing oils produced asphalts more durable than the one from the soft flux, none was as durable as the asphalt produced from the hard flux. Thus, for the Kansas flux, processing changes seemed to accomplish more than the fluxing oils.

The effects of these four fluxing oils on the durabilities of the Tia Juana asphalts were less than the effects of processing to the harder flux.

The results presented above corroborate in more detail those reported by Mertens and Greenfeld (5) and stress the importance of matching the fluxing oil to the flux with which it is to be used.

Certain materials when added to fluxes in small concentrations before blowing produce large changes in the blown asphalts. These materials have come to be known as catalysts, even though they are, in many cases, consumed in the reaction. Abraham (7) lists large numbers of these for accelerating the blowing reaction, increasing or decreasing the penetrations, increasing the ductility and improving the weathering characteristics of the blown asphalts. A few of these many types of materials have been investigated.

Ferric chloride, typical of the Lewis Acids, has been used for many years to accelerate blowing, increase penetrations and improve the fire tests of the finished products. While its advantages are many, it has two inherent deficiencies, which have seemed to limit its use. Ferric chloride tends to accelerate photooxidation (8) and asphalts containing ferric chloride have been reported to be corrosive under some circumstances (9).

In this study, the four fluxes were each blown with 1% ferric chloride both with and without agitation. The effects on blowing time were amazing (Table 6). The air rate of 150 ft^3/TM could not be used with the California flux because the reaction was too rapid; thus, the air rate was halved and the blowing time was still reduced to 20-25% of normal. The penetrations were increased appreciably, but the low-temperature penetrations were not raised enough to meet the specification.

Ferric chloride (1%) also accelerated the blowing of the fluxes from the other three sources. Kansas flux with 1% ferric chloride blew to 219°F softening point in 4 minutes with, and 19 minutes without, agitation instead of 62 and 202 minutes, respectively. The Talco and Tia Juana fluxes responded similarly, but to different degrees. The penetrations at all three temperatures were increased for the Kansas, Talco and Tia Juana asphalts. The asphalts made from the Kansas and Tia Juana fluxes actually had penetrations exceeding the specification maxima.

TABLE 6.

EFFECT OF CATALYSTS ON PHYSICAL PROPERTIES OF ASPHALTS

Flux Composition	Blown Without Agitation at 475°F, 150 ft³/Ton Min					Blown With Agitation at 475°F, 150 ft³/Ton Min				
			Penetrations					Penetrations		
	Time Min.	S.P. °F	at 32°F 1/10 mm	at 77°F 1/10 mm	at 115°F 1/10 mm	Time Min.	S.P. °F	at 32°F 1/10 mm	at 77°F 1/10 mm	at 115°F 1/10 mm
California	240	217	4	8	18	61	223	6	16	25
+ 1% Ferric Chloride	50 1/	223	8	18	23	13 1/	222	9	17	32
+ 1% Phosphoric Acid	146	217	12	21	38	35 1/	222	12	27	44
+ 1% Phytic Acid	245 1/	219	7	15	24	33 1/	221	10	23	39
+ 1% PMDA						45 1/	221	10	17	31
+ 1% TMA	109	217	7	14	33	45 1/	223	8	16	26
+ 1% VR-1 Acid	186	217	6	10	27	64 1/	219	7	13	28
Kansas (Hard)	202	219	9	18	36	62 1/	219	12	19	34
+ 1% Ferric Chloride	19	219	16	34	54	4	221	15	30	58
+ 1% Phosphoric Acid	240	223	14	25	45	41 1/	219	12	21	50
+ 1% Phytic Acid	217	219	15	25	44	46	221	11	22	40
+ 1% PMDA						27	217	15	25	40
+ 1% TMA	60	217	13	25	41	30	219	8	13	27
Kansas (Soft)	330	221	11	19	29	68	221	12	20	34
Talco (Hard)	212	219	12	17	32	61 1/	217	11	18	35
+ 1% Ferric Chloride	52	219	14	22	41	16 1/	221	12	22	39
+ 1% Phosphoric Acid	243	217	13	23	38	63 1/	223	13	23	38
+ 1% Phytic Acid	225	219	13	19	35	67 1/	221	14	20	34
+ 1% PMDA	241	217	9	16	30	54 1/	221	10	17	28
+ 1% TMA	180	217	9	17	35	45 1/	217	10	15	28
+ 1% VR-1 Acid	317	217	8	13	27	93 1/	221	10	13	20
Talco (Soft)	317	219	12	19	36	65 1/	217	13	20	34
Tia Juana (Hard)	374 1/	217	9	16	30	68 1/	219	11	16	31
+ 1% Ferric Chloride	51 1/	217	14	25	46	15 1/	221	14	27	43
+ 1% Phosphoric Acid	367 1/	217	12	21	38	45 1/	223	15	27	45
+ 1% Phytic Acid	360 1/	217	13	23	43	52 1/	217	14	25	46
+ 1% PMDA	231 1/	219	9	15	33	44 1/	217	11	19	36
+ 1% TMA	137	217	10	22	35	41 1/	219	12	20	35
+ 1% VR-1 Acid	428 1/	217	9	21	34	73 1/	219	9	15	30
Tia Juana (Soft)	390 1/	217	14	21	38	64 1/	217	14	21	37

PMDA = Pyromellitic Dianhydride
TMA = Trimellitic Anhydride
1/ Air Rate 75 ft³/Ton Min

The effects of the ferric chloride on durability were not uniform. Appreciable improvement was observed only in the case of Tia Juana asphalt blown without agitation. Kansas asphalt blown with agitation, on the other hand, had its durability seriously impaired.

Campbell and Wright (8) presented evidence to show that ferric chloride might be an oxidation inhibitor in the absence of light and an oxidation promoter in its presence. It appeared that the rapid increase in softening point during blowing is the result of other than reactions in which oxygen is taken into the molecules in asphalt. They describe alkylation and polymerization reactions which can account for the increases in softening point without the addition of oxygen. The other, and generally conceded most important, reaction during blowing is condensation, or dehydrogenation, which may account for the large quantities of water formed during blowing. All of these reactions can be accelerated by ferric chloride, but the latter also requires oxygen. This may partially explain why despite the fact that little oxygen remains in the blown asphalt, blowing with nitrogen requires a much longer time than blowing with air.

Based on a paper by Goppel and Knotnerus (10), an appreciable amount of ester formation occurred during blowing, especially at the lower blowing temperatures. Recently this conclusion was challenged by Campbell and Wright (11) because they were unable to find reinforcement of the carbonyl absorbance at 1700 cm^{-1} by the addition of model ester compounds to asphalts. Whether or not ester formation occurs to any appreciable degree, certain acids and anhydrides added to asphalt fluxes before blowing modify the blown asphalt. A number of these materials will be discussed.

Phosphoric acid, or phosphorus pentoxide, has been used for many years to modify asphalts; a number of patents have been issued on its use (7) and a number of articles have been published (12).

Phosphoric acid is probably not a catalyst (12a), but enters into the reaction and cannot be extracted from the asphalt with water (12a). As long as there was uncombined phosphoric acid or anhydride present, the reaction rate was higher than normal; when it was exhausted, the reaction rate dropped appreciably. When concentrations lower than one percent were used, this deceleration was always observed before

the coating-grade softening point was attained; at the one percent level the point of exhaustion was not reached with all fluxes. Thus, some of the runs show an appreciable shortening in blowing time while others show an actual increase. The California asphalt was improved by the use of one percent phosphoric acid. The penetrations were raised into the specification ranges and the blowing times were reduced about 40%. The durabilities were increased between 30 and 80%. The penetrations of all of the other asphalts were also increased, but not as spectacularly as in the case of the California asphalt. The blowing times of Kansas and Tia Juana fluxes were reduced when agitation was used, but not in the absence of agitation. The blowing times of the Talco flux were increased. The durabilities of the Kansas asphalts were increased, but those of the Talco and Tia Juana asphalts, not affected. Thus, while phosphoric acid always increased the penetrations of blown asphalts, it had mixed effects on their blowing times and durabilities.

Phytic acid, the hexaphosphoric acid ester of inositol, offers many more reaction sites per molecule than does phosphoric acid. If ester formation were the route by which asphalt hardening occurred, this material with its twelve reactive sites could conceivably become the nucleus of large molecules. However, in practice it reacted very much like phosphoric acid at the same weight concentration. The increases in penetrations were about the same, as were the blowing times. However, in all but the Talco asphalts blown with agitation, the durability increase was greater for the asphalts produced with phytic acid. The improvements ranged from an insignificant single day to 16 days.

Polyfunctional carboxylic acids and anhydrides are readily available and more like the acids that would be formed by the oxidation of hydrocarbons. While many carboxylic acids are notoriously heat sensitive, some remain stable for periods of time under the conditions of blowing. The pyromellitic dianhydride is tetrafunctional, the trimellitic anhydride is trifunctional and the VR-1 acids larely difunctional. All of these acids could form polyester type polymers with alcohols either present in the flux or generated during blowing. These acids and anhydrides did not produce the same effects on all four fluxes. There was no trend in any asphalt related to the number of carboxyl groups per molecule. However, for three of the four fluxes, one percent of any of these compounds tended to raise the penetrations of the blown asphalts. Talco asphalts tended to have reduced penetrations. Similarly, the blowing times were usually, but not always, decreased by these additives. In extreme instances, the blowing time was halved.

These carboxylic acids and anhydrides also produced mixed effects on the durabilities of the asphalts. These ranged from an increase to 100 days for the durability of the Tia Juana asphalt blown with TMA withoug agitation to a decrease to 60 days of the Kansas asphalt blown with TMA with agitation. TMA was the most effective additive for improving the durability of the Tia Juana asphalt; phytic acid was next most effective. Phytic acid was also most effective at the one percent level for improving the durabilities of the California and Kansas asphalts. While none of these materials improved the durability of the Talco asphalts blown with agitation, the phytic acid and the carboxylic additives improved the durabilities of the Talco asphalts blown without agitation.

In recent years an effort has been made to modify asphalt through the addition of polymers. Asphalt- and coal tar-epoxy coatings are on the market. Various elastomers have been mixed with asphalt for paving (13) and laminating uses. Mertens and Greenfeld (5) reported on the effects of a hydrocarbon polymer on the durability of asphalts.

Polymers added to the extent of 5% of the asphalt produced varied, but not large, changes in the penetrations (Table 7). The only polymer that changed the penetrations of the California asphalt sufficiently to bring it "into grade" was Saran. Saran also improved the susceptibility appreciably, but it simultaneously dropped the durability from 62 to 37 days. The epoxy resin improved the durability of the California asphalt to 77 days even though it did not raise the penetrations sufficiently to meet the specification. Poly(vinyl formal) and poly (vinyl butral) had no effect on the penetrations, but increased the durabilities of the California asphalts to 96 and 100 days, respectively.

None of the three polymers used improved the penetrations of the Kansas asphalt more than two units; all of them actually decreased the high temperature penetration. Simularly, none of them increased the durabilities; the Silicone reduced the durability by more than 50%. It was obvious that the Silicone did not react with the asphalt, for it appeared throughout the asphalt as a white powder. The variations in durability among the individual specimens were very large.

All of the polymers decreased the penetrations of the Talco asphalts from two to nine units. The effect on durability was small except for that of the poly(vinyl butral); it increased the durability by 23 percent.

TABLE 7.

EFFECT OF POLYMERS ON PHYSICAL PROPERTIES OF ASPHALTS

Flux Composition	Blown Withouth Agitation at 475°F, 150 ft³/Ton Min					Blown With Agitation at 475°F, 75 ft³/Ton Min				
			Penetrations					Penetrations		
	Time Min.	S.P. °F	at 32°F 1/10 mm	at 77°F 1/10 mm	at 115°F 1/10 mm	Time Min.	S.P. °F	at 32°F 1/10 mm	at 77°F 1/10 mm	at 115°F 1/10 mm
California	240	217	4	8	18	69	221	7	12	26
+ 5% Epoxy	293	217	6	10	23	90	223	6	14	23
+ 5% Neoprene	300[1]	225	3	9	16	60	225	9	17	29
+ 5% Saran						75	225	13	19	23
+ 5% Silicone	203	217	8	12	26	83[2]	221	8	16	27
+ 5% Vinyl Butral						72[2]	217	7	12	24
+ 5% Vinyl Formal						77[2]	217	8	13	25
Kansas (Hard)	202	219	9	18	36					
+ 5% Epoxy	536	219	10	15	27					
+ 5% Neoprene	261	225	8	17	29					
+ 5% Silicone	194	217	11	19	33					
Kansas (Soft)	330	221	11	19	29					
Talco (Hard)	212	219	12	17	32					
+ 5% Epoxy	435	217	9	15	30					
+ 5% Neoprene	192	221	10	15	28					
+ 5% Silicone	425	219	7	14	26					
+ 5% Vinyl Butral	264	217	8	13	23					
Talco (Soft)	317	219	12	19	36					
Tia Juana (Hard)	374[1]	217	9	16	30					
+ 5% Epoxy	400	219	7	11	22					
+ 5% Neoprene			Curdles							
+ 5% Silicone	259	217	11	19	30					
Tia Juana (Soft)	206	217	13	22	37					

[1] Air Rate = 75 ft^3/Ton Min

[2] Air Rate = 150 ft^3/Ton Min

TABLE 8. EFFECT OF ADDITIVES ON DURABILITY

DURABILITY (51-9c), DAYS

Asphalt	California		Kansas		Talco		Tia Juana	
Blowing Conditions Additive	A	B	A	B	A	B	A	B
FLUXING OILS								
Alone (Hard)	45	62	81	100	57	62	68	80
+ 5% ERL	38	40	73	58	72	41	61 1/	65
+ 5% WRL	63	58	93	84	86	55	58 1/	68
+ 5% MCBS	58	41	87	91	76	83	71 1/	72
+ 5% WBS	59	47	93	87	84	63	55 1/	67
Alone (Soft)	-	-	65	81	56	47	59 1/	50
"CATALYSTS"								
Alone (Hard)	45	62	81	100	57	62	68	80
+ 1% FeCl$_3$	54 1/	54	62	64	61	58	85 1/	68
+ 1% H_3PO_4	84	81	97	106	63	60	71 1/	82
+ 1% Phytic Acid	89 1/	85	110	107 2/	72	59	85 1/	98
+ 1% PMDA	-	53	-	85 2/	74	48	86 1/	69
+ 1% TMA	77	70	77	60 2/	74	62	100	74
+ 1% VR-1	76	60	-	-	73	47	82	73
Alone (Soft)	-	-	65	81	56	47	59 1/	50
POLYMERS								
Alone (Hard)	45	62	81	100	57	62	68	80
+ 5% Epoxy	77	77 2/	87	-	46	-	63	-
+ 5% Neoprene	45	44 2/	82	-	64	-	Curdles	-
+ 5% Saran	-	37 2/	-	-	-	-	-	-
+ 5% Silicone	48	34 2/	34	-	51	-	57	-
+ 5% Vinyl Butral	-	100 2/	-	-	70	-	-	-
+ 5% Vinyl Formal	-	96 2/	-	-	-	-	-	-
Alone (Soft)	-	-	65	81	56	47	59 1/	50

Blowing Conditions. A = 475°F, 0 r.p.m., 150 ft^3/Ton Min.
B = 475°F, 1400 r.p.m., 75 ft^3/Ton Min.

1/ 75 ft^3/Ton Min

2/ 150 ft^3/Ton Min

The Neoprene latex curdled when added to the Tia Juana asphalt at a number of different temperatures, even though no difficulty was encountered mixing it with the other three asphalts. The epoxy resin reduced the penetrations of Tia Juana asphalt while Silicone increased them. Both reduced the durability slightly.

As reported by Mertens and Greenfeld (5) for a hydrocarbon polymer in asphalts, the effects of these polymers on the asphalts were quite irregular. Each asphalt-polymer system must be evaluated on its own merits.

6. SUMMARY AND CONCLUSIONS

The properties of blown asphalts can be modified by the addition of small quantities of fluxing oils, catalysts or polymers to their fluxes before blowing. The effects are not uniformly the same, but vary with both the source of the flux and the processing. Deleterious as well as beneficial results can be obtained; it is critically important to evaluate each flux-additive system on its own merits.

The improvements in durability produced by processing reported earlier (2f) were extended by the use of additives. The most durable products produced from each flux with additives were:

Flux	Additive	Concentration	Blowing Conditions	Durability (51-9C)
		%		Days
California	Poly(vinyl butral)	5	B	100
California	Poly(vinyl formal)	5	B	96
Kansas	Phytic acid	1	A	110
Kansas	Phytic acid	1	B	107
Talco	Western Reclaimed Lube	5	A	86
Talco	Western Bright Stock	5	A	84
Talco	Mid-Cont. Bright Stock	5	B	83
Tia Juana	Trimellitic anhydride	1	A	100

A = 475°F, 0 r.p.m., 150 ft^3/Ton-Min.
B = 475°F, 1400 r.p.m., 75 ft^3/Ton-Min.

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